

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 5/10/96	3. REPORT TYPE AND DATES COVERED Final Report (06/01/92 - 12/31/95)	
4. TITLE AND SUBTITLE Bio-Mimetic Routes to Optical and Electronic Composites and Ceramics			5. FUNDING NUMBERS F49620-92-J-0239 61102F 2303/DS	
6. AUTHOR(S) Dr. Paul Calvert and Dunbar Birnie				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Materials Science and Engineering College of Engineering and Mines The University of Arizona Tucson, AZ 85721			8. PERFORMING ORGANIZATION REPORT NUMBER AFOSR-TR-96 0243	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Office of Scientific Research/MC Building 410 Bolling AFB, DC 20332-6448 Dr Hedberg				
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for Public Release - Distribution is unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) <u>Abstract</u> Polymer films containing non-centrosymmetric crystals have been prepared and characterized by second harmonic generation. Combinations of water-soluble polymers and KDP or ADP produced good films. Efforts were made to extend this method to lead titanate, lead zirconate titanate and potassium titanyl phosphate. These materials were successfully produced as crystalline thin films via sol-gel chemistry with a high temperature annealing step. Composite films could be produced of these materials in amorphous form in polymers, but we did not yet succeed in crystallizing the inorganic material under hydrothermal conditions within the polymer. Bacterial threads, which have a highly phosphated cell wall, were also used as a support for the controlled growth of KDP powders and the resultant composites characterized by SHG.			19960523 200	
14. SUBJECT TERMS			15. NUMBER OF PAGES 16	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Unlimited	

FINAL REPORT TO AFOSR

For June 1992-December 1995

BIO-MIMETIC COMPOSITES FOR ELECTRICAL AND OPTICAL PROPERTIES

Paul Calvert, Dunbar Birnie and Neil Mendelson

University of Arizona

F49620-92-J-0239

Abstract

Polymer films containing non-centrosymmetric crystals have been prepared and characterized by second harmonic generation. Combinations of water-soluble polymers and KDP or ADP produced good films. Efforts were made to extend this method to lead titanate, lead zirconate titanate and potassium titanyl phosphate. These materials were successfully produced as crystalline thin films via sol-gel chemistry with a high temperature annealing step. Composite films could be produced of these materials in amorphous form in polymers, but we did not yet succeed in crystallizing the inorganic material under hydrothermal conditions within the polymer.

Bacterial threads, which have a highly phosphated cell wall, were also used as a support for the controlled growth of KDP powders and the resultant composites characterized by SHG.

BIO-MIMETIC COMPOSITES FOR ELECTRICAL AND OPTICAL PROPERTIES

1. Introduction

There is a need for sensor systems to monitor aircraft structures and other systems continuously during operation. While there is an abundance of sensor materials and devices, it is not clear how these can be integrated into a structure in large numbers. Single devices can be attached to the outside or inside of a metal or composite structure and coupled back to monitoring equipment. However attachment of one rigid material to another leads to interfacial stresses so that a long life can only be achieved with relatively massive fixtures.

A desirable model is human skin with large numbers of sensors integrated into the surface and coupled through a network of nerves back to a central processor. A sensible first approach to this would be an organic coating containing distributed sensors for metal structures, or an integrated sensor layer in composite structures. Current inorganic piezoelectric stress sensors are brittle ceramic sheets which do not lend themselves to such integration. These perovskite materials can be formed as thin films on a surface via chemical deposition methods but these require annealing at around 600°C which would destroy any organic matrix. Organic polymers such as polyvinylidene fluoride offer more compatibility, but the need for cold drawing means that these materials must be preformed and then embedded in the composite or coating.

The approach explored in this work is to grow the piezoelectric sensor phase in the organic matrix. In past work we have formed crystalline organic non-linear optical crystals in a polymer matrix and have shown how the matrix can be used to control the size and orientation of the crystals¹. These organic materials have a high vapor pressure, so the composites have no long-term stability. Hence it is desirable instead to grow inorganic materials in a polymer matrix.

The growth of inorganic crystals under the control of a polymer matrix is achieved par excellence in biomineralization. Mineralized biological tissues show very sophisticated control of crystal form in order to optimize the properties of the composite². This includes sensing organs such as the inner ear and the optical structures that give rise to diffractive colors of insects.

The goals of this project were to develop routes to form inorganic piezoelectric crystals in polymer matrices under conditions compatible with the formation of tough coatings or composites. Crystal growth in and on bacterial cell walls was also studied since these contain very high levels of phosphated anionic polymers which should provide excellent substrates for many inorganic crystals. The formation of these composites was monitored by second harmonic generation since this provides a probe for the non-centrosymmetric crystals without the need for application of electrodes and poling to measure piezoelectricity.

1. Experimental details

2.1 Preparation of SHG films

Second harmonic generating (SHG) films were made utilizing phase separation of solutes due to solvent evaporation. Potassium dihydrogen phosphate (KDP) and ammonium dihydrogen

phosphate (ADP) were used as the nonorganic SHG phase. Since KDP and ADP are water soluble and rapidly precipitate out of solution in the presence of common organic solvents, the list of compatible polymers was short. For the composites, samples of the following polymers were tried: polyethylene oxide (PEO), hydroxyethylcellulose (HEC), polyacrylamide (PA), and polyacrylic acid (PAA). Initial solutions were made by dissolving the polymers in boiling water to make a 10 wt% solution. The solutions were then mixed with an equal amount of a 10 wt% solution of either KDP or ADP in water.

Two application techniques were used. Solutions were spin-coated onto glass substrates at approximately 1500 rpm until dried. Multiple layers (8-10) were applied. Samples were also made by casting the solutions onto glass microscope slides and allowing them to air dry. Again, several (2-3) layers were applied with some having a final coat of the plain polymer solution.

From the results of these initial coatings, polyacrylic acid no longer was used. The concentration of KDP and ADP in the starting solutions was also too great. Aqueous solutions of 2.5 wt% polymer (PEO, PA, and HEC) and 2.5 wt% ADP or KDP were dipcoated onto glass slides at a withdrawal rate of 15 mm/s. These would result in final composites containing 50 wt% of the inorganic salt. The films were dried flat in air. Polymer solutions (2.5 wt%) without ADP and KDP were also coated in the same manner.

2.2 PZT sol-gel

Lead zirconate titanate (PZT) was chosen as one of the piezoelectric components of the composites. Ideally, the PZT crystals would grow in-situ throughout a polymer matrix. The major obstacle was the crystallization of PZT at low temperatures. Therefore, low temperature (below $\sim 250^{\circ}\text{C}$) synthesis through hydrothermal treatment was studied first. The first route tried for forming PZT crystals used a PZT sol-gel solution consisting of lead (II) 2-ethyl-hexanoate in naphtha, zirconium isopropoxide, titanium isopropoxide, and propanol³. The solution was partially hydrolyzed with dilute acetic acid to a final pH of 5.8 and refluxed at 90°C for 24 hours.

Lead titanate (PT) was also investigated. A series of 0.5 M lead titanate sol-gel solutions were created using titanium oxide acetyl-acetonate, lead acetate, and 2-methoxyethanol⁴. Water-to-metal ratios of 1 to 5 were used with final solution pH's ranging from 1 to 11 depending on whether a catalyst of HCl or NH_4OH was used and its concentration.

Samples were dipcoated onto soda-lime glass substrates from the PZT and PT solutions, dried, and steam treated in hermetically sealed test tubes at 160°C in an attempt to achieve crystallization. Additional samples were coated onto pieces of silicon wafers and fired to 600°C . The steam environments were acidic, basic, neutral, and lead containing. Powders dried from the solutions were processed in a manner similar to those of the films.

2.3 Polymer/sol-gel films

For growth of the crystals in the polymer matrix, a polymer/sol-gel solution was then made by adding the PT sol-gel drop-wise into a solution of polyvinyl chloride in tetrahydrofuran.

If the sol-gel was added very slowly and allowed to mix completely in between drops, the solution did not form precipitants. Films were cast of the solution and allowed to dry. They then were steam treated in sealed test tubes under the same conditions as the sol-gel films.

2.4 Hydrothermal synthesis of PT

A precipitation process of forming crystalline lead titanate was also tried. Hydrothermal processing is a method of crystal growth used mainly in geosciences. Chemical species that are not soluble at atmospheric conditions can be under increased pressure and in the presence of a mineralizer. A super-saturated solution forms from which crystals precipitate out and grow. Success hinges on the proper combination of solvent, pressure, pH, and temperature. Also, the crystal phase must be thermodynamically favored under chosen conditions, and a vessel suitable for the necessary temperatures and pressures has to be used.

Hydrated PbO was precipitated out from aqueous lead nitrate or lead acetate solutions, and hydrated TiO₂ was precipitated from titanium butoxide and titanium isopropoxide/ethanol solutions by combining all solutions with dilute potassium hydroxide. KOH was used as a mineralizer at varying concentrations as the mineralizer to enhance crystallization. The resulting fine white powders in a water/ethanol were hydrothermally treated in a 500ml, 316-Stainless Steel Zipperclave by Autoclave Engineers. Reaction temperatures ranged from 120°-250°C and pressures from 10 psi to 225 psi under a nitrogen environment for 2 to 120 hours^{5,6,7}. The powders were then filtered out, washed with dilute acetic acid, deionized water, or dilute KOH, and dried.

Polymer films containing lead titanate precursors were also autoclaved. Polyvinyl chloride was dissolved in THF (5wt%) with equimolar amounts of Pb(II) 2-ethylhexanoate and titanium butoxide to form a clear, light brown solution. Films were formed by dipcoating at speeds of 3-17 mm/s and by syringing lines of solution on glass slides. They were then autoclaved in a solution of lead nitrate and acetic acid at 175°C for 24 hours. A solution was also made of 5 wt% PMMA in dimethylacetamide with equimolar lead nitrate and titanium butoxide. Since the titanium butoxide was immiscible in DMAC, the solution was mixed rapidly to form an emulsion and immediately syringed onto a glass slide. A solution of lead acetate and acetic acid was used as the autoclaving solution at 150°C for 20 hours. Additional films were cast using a DMAC/PMMA solution made with titanium isopropoxide. The same autoclaving conditions as the other PMMA samples were used, but the experiment was run for 120 hours.

2.5 KTP sol-gel

A 0.5 M potassium titanyl phosphate sol-gel solution was prepared by combining equal molar ratios of titanium isopropoxide, 2,4-pentanedione, tributyl phosphate, and potassium tert-butoxide^{7,8}. A partial hydrolysis of 2.5 molar equivalent water was used. After mixing the sol-gel for several hours, 2,2-azobis-2-methylpropionitrile and 10 vol% ethylene glycol dimethacrylate

were added, and the solution was heated at 70°C until solidification. Resulting powders were fired from 550°C to 650°C to achieve crystallization.

2.6 Bionites

Initially all bionites were made by the addition of ions (sources: calcium phosphate, iron sulfate, potassium dihydrogen phosphate) to the bacterial growth medium (tryptose-beef extract) in which the web-form cultures of *Bacillus subtilis* had been grown. When the webs were drawn later into threads, crystals were trapped in the drawing process and new crystals formed during the drying of the threads.

To remove the growth medium and permit cleaner chemistry, a method was devised to produce webs in cultures grown in funnels. Growth medium could be drained from these cultures and replaced with desired ion solutions while maintaining web integrity so that later the products could be drawn.

The viability of the bacterial cells in the threads and bionites was studied using a bacterial viability staining kit that distinguishes live cells from dead cells on the basis of a fluorescent reaction governed by a permeability difference between live and dead cells. Also, *in situ* purification protocols were developed that permit removal of virtually all the cell contents yet retain the ability to draw the now hollow cell walls into a thread. This was accomplished by lipid extraction and digestion with nucleases and protease thus avoiding destructive detergents and sonification.

3. Results and Discussion

3.1 Phosphate composites

SEM micrographs of spin-coated 10wt% polyethylene oxide/KDP films reveal a structure of polymer with holes on the order of 3 microns (figure 1). At the base of the holes are KDP crystals. Samples made without spin-coating have visible macroscopic KDP crystals in the polymer without any apparent separation. SHG was visible to the eye in the cast samples, but not in the spin-coated ones.

Hydroxyethylcellulose produces the most coherent films using both ADP and KDP. Again, cast samples have visible crystals and they are well adhered to the polymer. Spin-coated KDP films consist of small crystals with finer crystals radiating off the ends. There seems to be some degree of local orientation. ADP films appear to contain very fine agglomerated particles. Some birefringence was visible through crossed polarizers, reflecting orientation in the polymer induced by the spin-coating process. No visible SHG was observed for either KDP or ADP films. The films have high strength, which increases with thickness, and they can easily be peeled off of the substrate.

Polyacrylic acid solutions spin-coat poorly because the polymer does not wet the glass well. KDP or ADP crystals form on the substrate but there is little polymer left. Cast samples, in

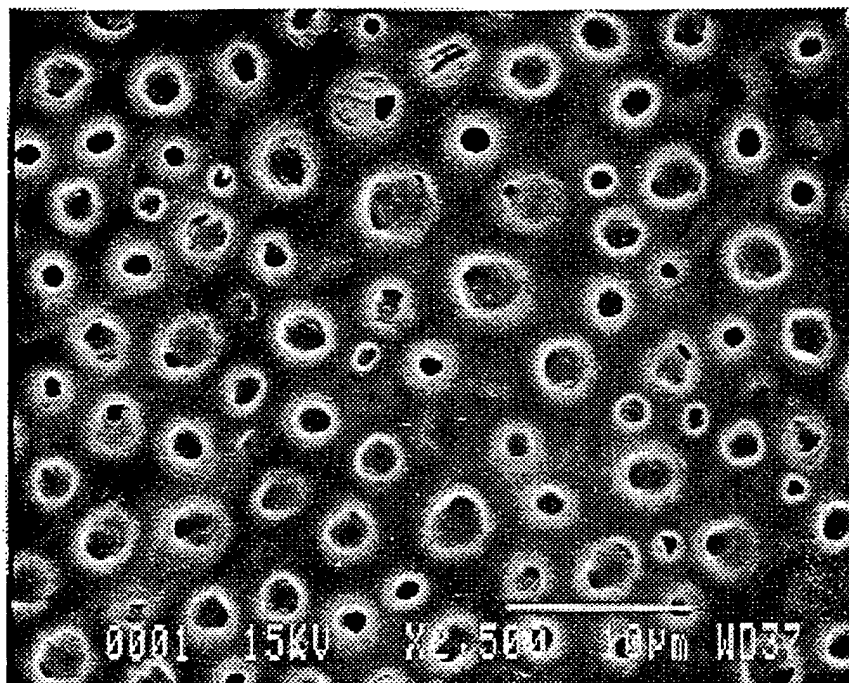


Figure 1: SEM photo of spin-coated 10wt% PEO/KDP film.

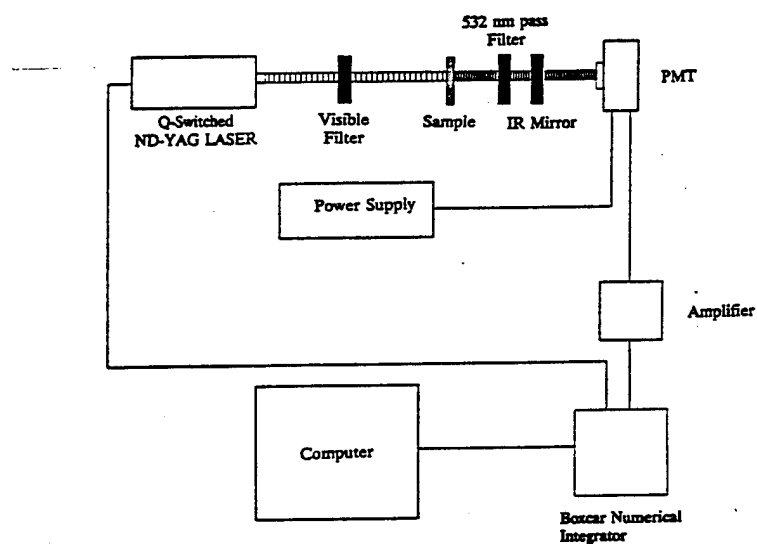


Figure 2: Layout of SHG characterization technique.

contrast, are more coherent especially when a plain polymer solution is allowed to dry over the previously formed composite films..

Polyacrylamide solutions spin-coat well and are very similar to the hydroxyethylcellulose films. In the cast samples, the crystals separate from the polymer by settling. SHG was detected in KDP samples using an oscilloscope.

The 2.5wt% ADP and KDP polymer composites were analyzed for SHG using a more sensitive characterization technique. SHG was measured using a Q-switched Nd-YAG laser (1060 nm, 16 Amps, 15kHz) coupled to a boxcar averager (figure 2). The films were held square with a photo-multiplier tube active at 532 nm and translated in and out of the beam. All of the ADP and KDP containing films exhibited visible and measurable SHG of similar values, as shown in figure 3 where the noise in the signal represents successive sections of sample being moved through the beam. The plain polymer films showed no SHG.

Optical microscopy (200X) of the 2.5wt% polymer films showed varying structures for the different compositions. Polyacrylamide/KDP films had small regions of KDP crystals oriented in the same direction. The groupings were roughly 5-10 microns in size and randomly oriented with regard to each other. Polyacrylamide/ADP films were very rough and had single crystals (2 μm x 6 μm) scattered throughout the polymer. Polyethyleneoxide/ADP and /KDP films had no visible features other than small clusters of tiny particles and it was unclear whether these were ADP/KDP crystals or undissolved polymer. HEC/KDP films had large regions of well formed, highly oriented crystals. HEC/ADP films had regions of ill-defined crystallinity in almost a cross-hatched pattern.

During the drying of these films, the first segregation process may be phase separation of the polymer or crystallization of the salt. A hole in the polymer surrounding small crystals suggests that the system has first phase separated into a concentrated salt solution and polymer. These porous films, as shown for PEO in figure 1, are undesirable. Where crystallization of the salt occurs first, the morphology of the composite films will primarily be a function of the viscosity of the solution at the point at which crystallization of the salt occurs. More viscous solutions give rise to smaller crystals. More concentrated starting solutions produce thicker films during the spin coating or dipping processes.

Overall orientation in films arises as a result of shear during the dipping or spinning process and reflects a higher viscosity at the time of deposition. Local orientation in clusters of crystals will reflect branching from a single nucleation site especially in the highly elongated crystals normally formed by ADP.

For piezoelectric applications, films would need to have electrodes applied. A tough film with good temperature resistance is needed. Crystals should be small and accommodated at high levels without embrittlement. Hydroxyethylcellulose would appear to be the best matrix and could be used at 50 wt% KDP or ADP.

3.2 PT sol-gel films

No crystallinity was detected by x-ray diffraction in dip-coated films made from the lead titanate sol-gel. This is believed to be because the films were too thin. Powders steam treated

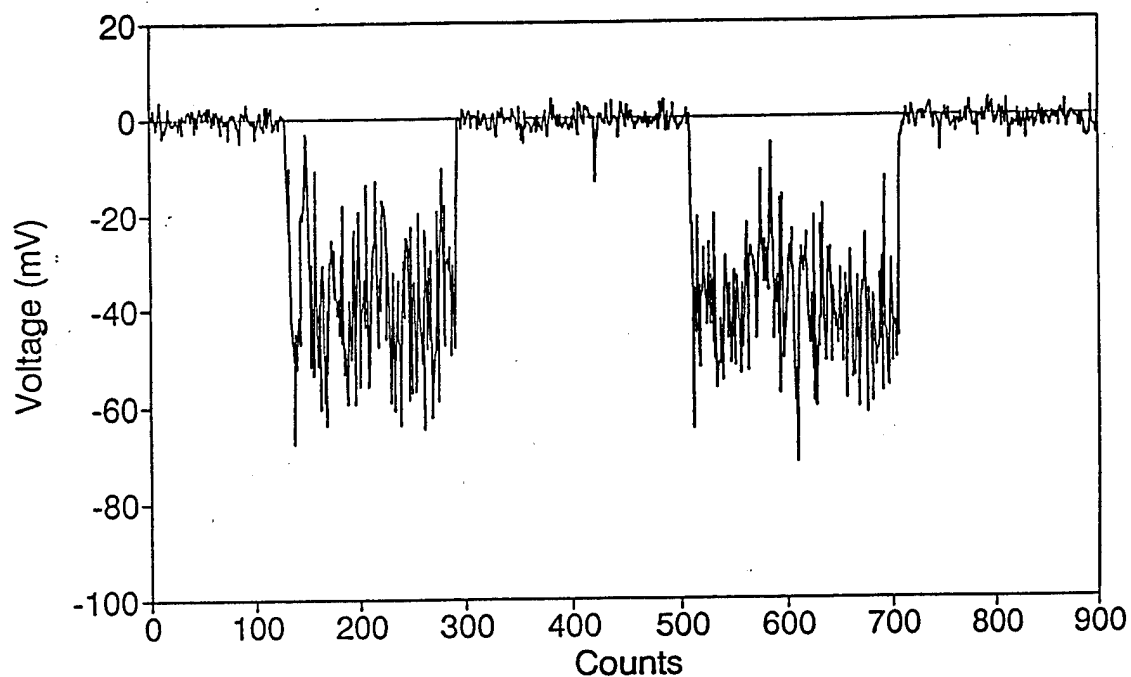


Figure 3: Second harmonic generation behavior of polyacrylamide/KDP film. Scan is typical of all SHG composites.

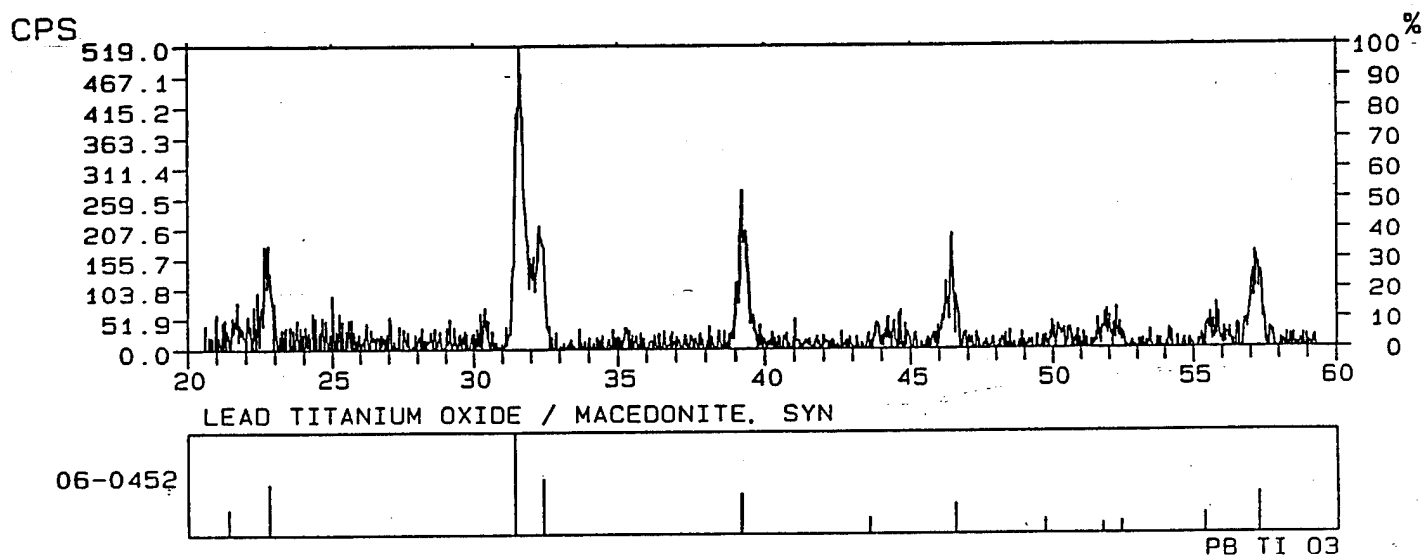


Figure 4: XRD pattern of lead titanate sol-gel powder fired at 600°C with JCPDF pattern for PbTiO_3 .

were amorphous, but powders fired to 600°C were crystalline and show a good match to the pattern of crystalline lead titanate (figure 4). No discernible differences in crystallinity were observed due to water content or pH.

3.3 Hydrothermal PT

Hydrothermally treated powders were amorphous as shown by the absence of distinct peaks in figure 5. The polyvinylchloride-lead titanate composite films had crystalline lead chloride as detected by x-ray diffraction. Lead chloride was used as a precursor but may also have arisen by reaction with the polyvinylchloride. The PMMA/Ti butoxide films were amorphous, while the PMMA/Ti isopropoxide films XRD patterns had a few peaks, but no pattern matches could be made to either lead titanate or to a form of titania.

3.4 KTP sol-gel films

KTP powders were x-ray crystalline, as shown in figure 6. The degree of crystallinity increased with firing temperature, as shown by the increasing peak height in figure 7 and the powders exhibited visible SHG (figure 8).

3.5 Bionites

In iron sulfate solutions, amorphous precipitates formed on the suspended web prior to drawing. The final bionite carries four layers of distinctly different iron crystal forms. The different forms have not yet been identified. Aligned needle-like KDP crystals formed in the bionites as seen in figure 9, while calcium phosphate crystals formed burr structures on the surface of the bionite (figure 10).

The viability staining kit showed that samples from webs prior to drawing contained 99%+ viable cells. After drawing the cells die rapidly. Less than 1% remain viable after 24 hours of drying. The method developed for *in situ* purification resulted in products that are about 95% pure cell wall.

4. Conclusions

The hydroxyethylcellulose/KDP and /ADP systems readily produce good films containing crystals that demonstrate second harmonic generation and could be used as piezoelectric composites. While there should be conditions under which the perovskites will form crystals in a polymer matrix we were not able to achieve this with lead titanate or lead zirconate titanate. Crystalline films can readily be formed at 600°C but more mild conditions are needed if an *in situ* route is to be found to grow these materials in polymers.

Bacterial fibers and mats provide a host for the growth of numerous minerals and salts. The process is complex since the drying and crystallization processes occur in parallel as in the spin-

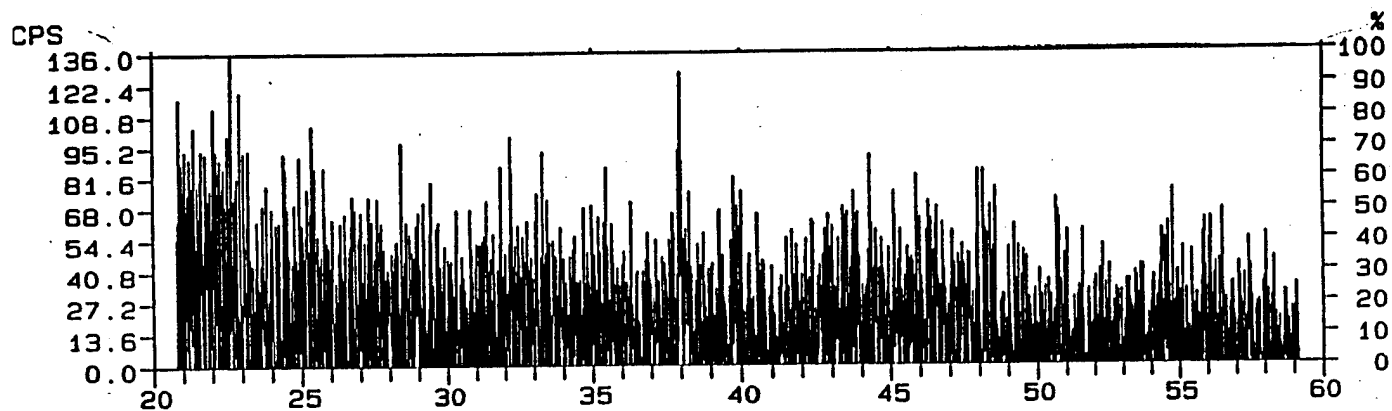


Figure 5: XRD pattern for hydrothermally treated lead titanate powder showing no discernible crystallization.

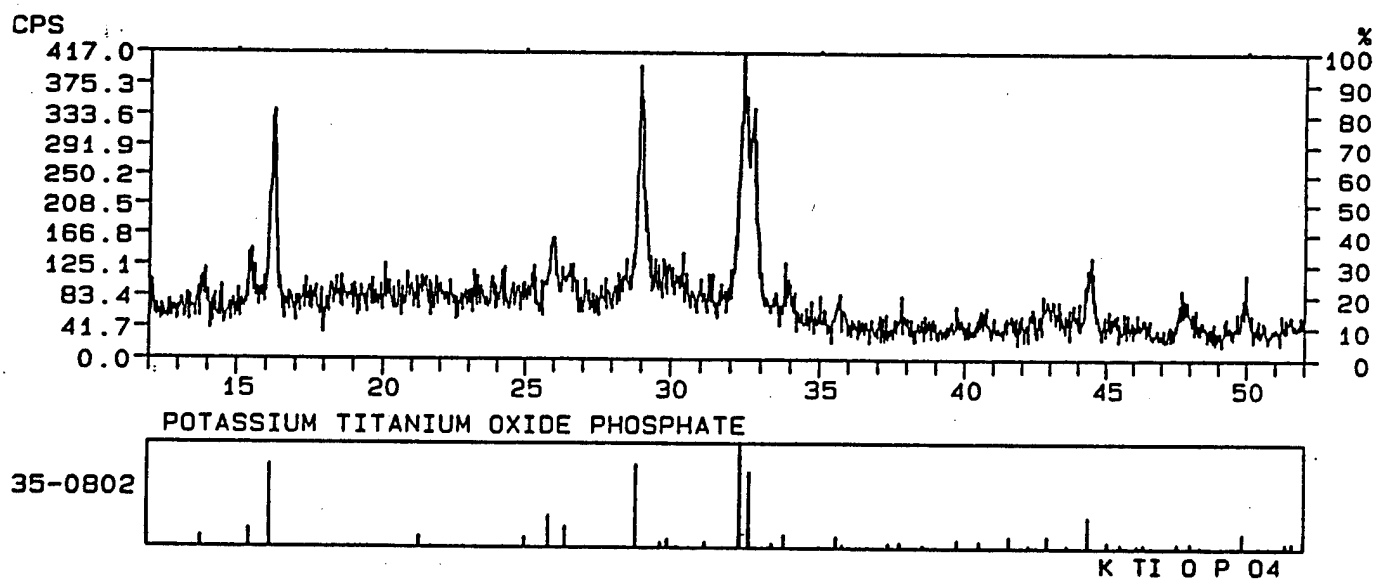


Figure 6: XRD scan of KTP with the JCPDF pattern.

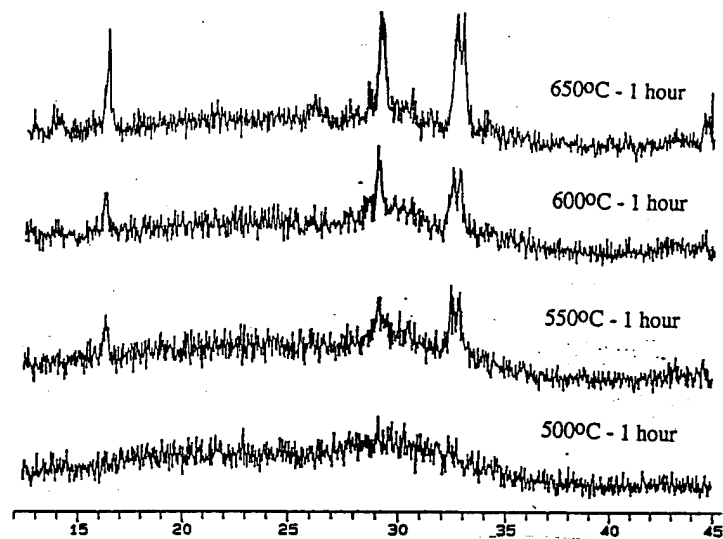


Figure 7: XRD scans of KTP with increasing firing temperatures. Note the formation of major peaks beginning at 550°C.

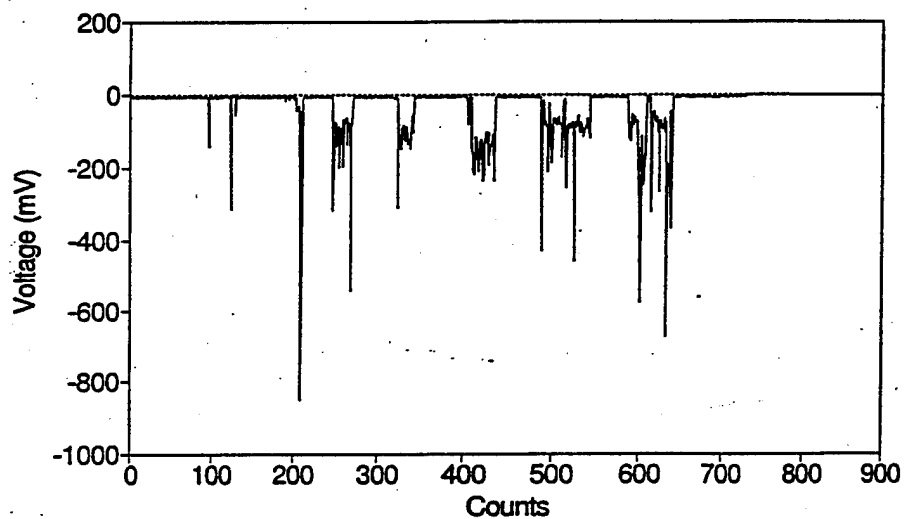


Figure 8: Second harmonic generation behavior of KTP thin films.

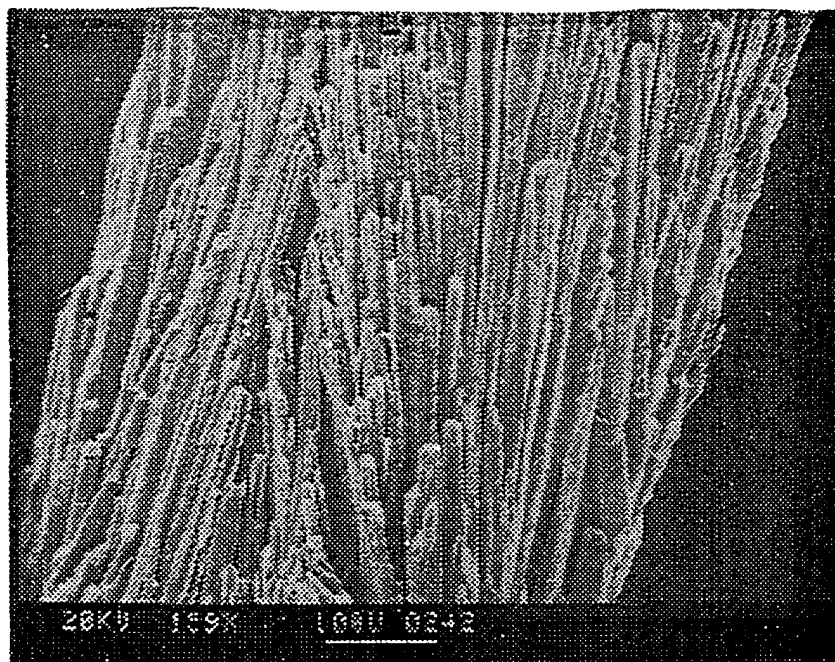


Figure 9: SEM photo of KDP bionite showing well aligned crystals.

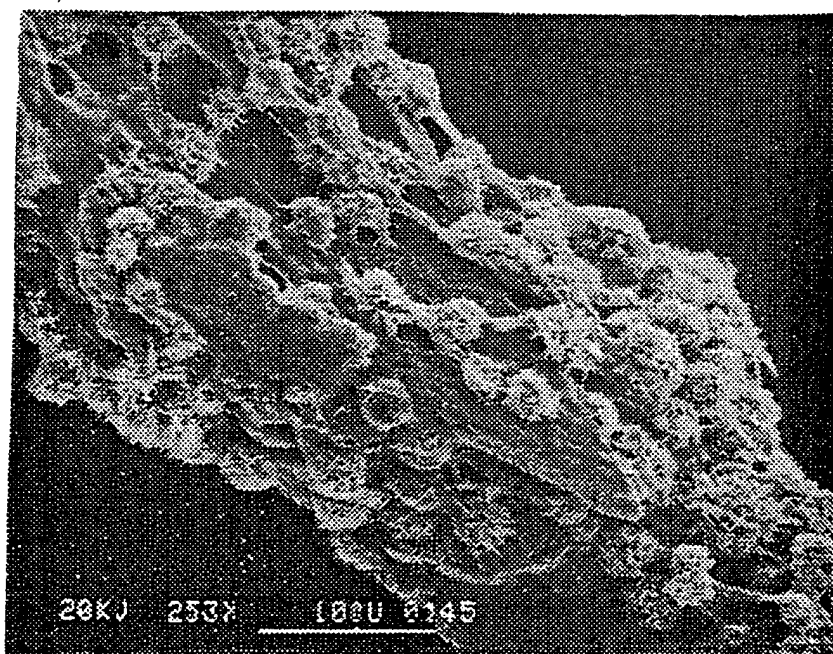


Figure 10: SEM photo of calcium phosphate bionites with brushite structure.

coated polymer films but the system now has a much more complex morphology. The method for purifying cell walls promises to provide a much cleaner system for the observation of controlled crystallization.

These approaches will be combined with our current work on freeform fabrication to deposit piezoelectric sensors and actuators as an integral part of solid structures.

5. References

1. N.Azoz, P.D.Calvert, M.Kadim, A.J.McCaffery and K.J.Seddon, "A novel high efficiency crystal/polymer composite material for non-linear optics", Nature **344**(49), 1990.
2. H.A. Lowenstam and S. Weiner, On Biomineralization, Oxford University Press, Oxford, 1989.
3. L.E. Sanchez, S. Wu and I.K. Naik, "Observations of ferroelectric polarization reversal in sol-gel processed very thin lead-zirconate-titanate films", Applied Physics Letters **56**(24), 1990.
4. S.J. Milne and S.H. Pyke, "Modified sol-gel process for the production of lead titanate films", Journal of the American Ceramic Society **74**(6), 1991.
5. H. Cheng, J. Ma and Z. Zhao, "Hydrothermal synthesis of PbO-TiO₂ solid solutions", Chemistry of Materials **6**(7), 1994.
6. G.A. Rossetti, D.J. Watson, R.E. Newnham and J.H. Adair, "Kinetics of the hydrothermal crystallization of the perovskite lead titanate", Journal of Crystal Growth **116**, 1992.
7. J.D. Vanderzeele, "Potassium titanyl phosphate:properties and new applications", Journal of the Optical Society of America B **6**(4), 1989.
8. M.A. Roelofs, "Sol-gel Synthesis of thin films of potassium titanyl phosphate for non-linear optical applications", Journal of Material Science Letters **12**, 1993.

Students supported

Lenette Raymond, graduate student, full year, MS expected 1996
Trey Huntoon, graduate student, obtained MS 1994, studying for PhD
Hugh Denham, graduate student, part year, studying for PhD
Research Technician biology, part time, continuing
Kate Sundahl, undergraduate, part year.
Evan Frank, undergraduate student, part time.
Aaron Hale, undergraduate, part time, finished
Kevin van den Bogert, part time, continuing
Shane Larkin, undergraduate, part time, continuing

Publications

Presented at MRS Meeting, November 1993

N.H. Mendelson, Bacterial Macrofibers and bionites. *Mater. Res. Soc. Symp. Proc.* **330**, 95-111 (1994).

P. Calvert, "Precipitation in and on polymers" *Mater. Res. Soc. Symp. Proc.* **330**, 79-88 (1994).

Presented at ICIM2, June 1994

P. Calvert "Intelligent composite materials by *in situ* precipitation", *Proceedings of the Second International Conference on Intelligent Materials*, C.A. Rogers and G.G. Wallace eds, Technomic Press Lancaster PA, 1994 pp. 259-264.

Presented at MRS meeting, April 1994

K. Stuffle, A. Mulligan, J. Lombardi, P. Calvert, B. Fabes, "Solid freebody forming of ceramics from polymerizable slurry", *Mater. Res. Soc. Symp. Proc.* **346**; 1027-1031 (1994).

Kevin Stuffle, Anthony Mulligan, Paul Calvert and John Lombardi, "Solid freebody forming from polymerizable slurry", *Solid freeform fabrication symposium proceedings*, Univ. of Texas, Austin, 1993, 60-63.

J.E. Mark and P.D. Calvert "Biomimetic, hybrid and in situ composites" *Mater. Sci Eng. C.* **1**, (1994) 175-186.

P. Calvert "Strategies for Biomimetic Mineralization" *Scripta Met.* **31** 977-982 (1994).

P.D. Calvert, "Polymers for new materials", *Polymer* **35** 4484-4488 (1994).

"Hierarchical structures in biology as a guide for new materials technology" National Acad. Press, 1994 (with 12 co-authors) pp.130.

J. Burdon, J. Szmania, P. Calvert, "Biomimetic composites" *Materials Research Society Symposium Proceedings* 1994, 351, 103-108 (1994).

P. Calvert, "Precipitation in and on polymers" *Mater. Res. Soc. Symp. Proc.*, 330, 79-88 (1994).

K. Stuffle, A. Mulligan, J. Lombardi, P. Calvert, B. Fabes, "Solid freebody forming of ceramics from polymerizable slurry" *Mater. Res. Soc. Symp. Proc.* 346; 1027-1031 (1994).

M. Oner and P. Calvert "The effect of architecture of acrylic polyelectrolytes on inhibition of oxalate crystallization" *Mater. Sci. Eng. C.* 2 93-102 (1994).

M. Kubo, W.C. Mollberg, A.B. Padias, H.K. Hall, Jr and P. Calvert, "Solubilization of peptides in water and hexane: synthesis of peptide-terminated poly(tert-butyl acrylate) and poly(acrylic acid) via living anionic polymerization." *Macromolecules* 28 838-843 (1995).

J. Burdon, J. Szmania, P. Calvert "Organic-Inorganic Hybrids with a Crystalline Polymer Matrix" in *Hybrid Organic-Inorganic Composites*, J.E. Mark et al. eds, ACS Symposia 585, 1995 pp.6-18, Am.Chem.Soc. Washington DC.

P. Calvert, "Biomimetic ceramics and hard composites" in *Biomimetics, Design and Processing of Materials*, M. Sarikaya & I.A.Aksay eds, AIP Press, Woodbury NY, 1995.

P. Calvert, R. Crockett, J. Lombardi, J. O'Kelly, K. Stuffle, "Extrusion methods for solid freeform fabrication" *Solid freeform fabrication symposium proceedings*, Univ. of Texas, Austin, 1994, 50-55.

P. Calvert "Solid freeform fabrication: a new process for composite materials", *Proc. 4th Japan Intl. SAMPE* eds. Z. Maekawa, E. Nakata, Y. Sakatani, 1995, pp.603-608.

P. Calvert, "Biomimetic Processing" in *Materials Science & Technology*, vol. 17B, ed. R.J. Brook, VCH Pubs, Weinheim, 1996, pp.51-82.

N. Mendelson, "Production and initial characterization of bionites: materials formed on a bacterial backbone", *Science* 258, 1993, pp.1633-1636.

Papers and Reports

Presented at MRS Meeting November 1994

Strategies for metal sulfide film formation, Joseph Cesarano III, Sandia National Laboratories; Paul Calvert; Lev Feigin, Institute of Crystallography, Moscow.

Solid freeform fabrication of biomimetic structures, Paul Calvert, Robert Crockett, John O'Kelly and John Lombardi.

Surface induced mineralization processes, Paul Calvert and Jeremy Burdon
Seminar to Advanced Materials Labs., Sandia National Labs., June 1994
Seminar at Hoechst Celanese, August 1994
Seminar, Dow Chemical Midland MI, Oct. 1993
Presentation at Schloessman Meeting, Max Planck Inst, Mainz, June 1995
Seminar at QUT, Brisbane, Australia, August 1995
Seminar at Dow Chemical, Freeport TX, Jan. 1995
Seminar at Durham University, England, June 1995
Presentation at ACS workshop on Hybrid materials, Feb. 1995
Seminar to Dept. of Chemical Engineering, University of Arizona, Jan 1995
Seminar to Composites symposium at Hughes Missile Co., Tucson

Consultations and Transitions

I have consulted extensively for Advanced Ceramics Research of Tucson who have applied for patents relating to our joint work on freeforming and are seeking to develop this as a business.
Technology Transfer & Patents